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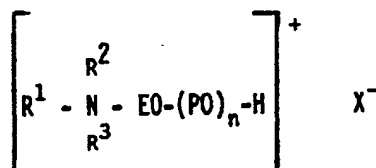
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(54) **Glyphosate compositions and their use.**

(57) The composition of the invention comprises a glyphosate herbicide and a quaternary ammonium compound the latter having the formula



wherein -EO- means an ethylene oxide radical and -PO- means a propylene oxide radical, R<sup>1</sup> and R<sup>2</sup> are each independently an alkyl group having from 1 to 3 carbon atoms; R<sup>3</sup> is an alkyl group having from 1 to 3 carbon atoms, a group having the formula (EO)<sub>m</sub>-H or a group having the formula EO-(PO)<sub>m</sub>-H; n (in a compound in which R<sup>3</sup> is an alkyl group) or n + m (in a compound in which R<sup>3</sup> is a group having the formula EO-(PO)<sub>m</sub>-H), has a value of from about 2 to about 20; and X<sup>-</sup> is a suitable anion.

EP 0 441 764 A1

## GLYPHOSATE COMPOSITIONS AND THEIR USE

This invention relates to an agriculturally acceptable glyphosate composition, more particularly to such compositions containing a glyphosate herbicide and a surfactant which enhances the herbicidal activity of the glyphosate herbicide. This invention also relates to the use of such compositions to kill or control unwanted and undesired vegetation. More particularly, such compositions contain a herbicidally effective amount of glyphosate.

Numerous studies have been made on the effect of additives on the herbicidal action of glyphosate. For example Wyrill and Burnside, *Weed Science*, Vol. 25 (1977), 275-287, examined solutions containing different classes of surfactant, including polyoxyethylene stearyl methyl ammonium chlorides containing respectively 2 and 15 oxyethylene units. Some classes of surfactant were more effective than others in enhancing the herbicidal effect of glyphosate (used as a solution of the isopropylamine salt), but Wyrill and Burnside concluded that an effective surfactant is a critical component of any glyphosate spray mixture.

Commercially sold glyphosate formulations generally contain a surfactant. These formulations are safe herbicidal formulations from the point of view of lack of toxicity and environmental acceptability. Moreover, the level of toxicity or irritancy which is shown in certain situations, for example commercial glyphosate formulations containing an ethoxylated tallow amine surfactant, which have some toxicity to aquatic life, is essentially due to the presence of the ethoxylated tallow amine surfactant and not due merely to the glyphosate itself.

This invention satisfies the need for an improved glyphosate formulation. In this invention currently employed surfactants are advantageously replaced by other surfactants which provide a similar efficacy enhancing effect to the herbicidal activity of glyphosate but also provide lower irritancy and toxicity than currently employed surfactants.

Ammonium salts such as ammonium sulphate (Turner and Loader, *Weed Research*, Vol. 20 (1980), 139-148) and ammonium thiocyanate (US-A-4 612 034) have also been shown to further enhance the herbicidal activity of glyphosate salt formulations containing surfactants.

EP-A-0 290 416 allegedly discloses improved glyphosate formulations containing alkoxyated amine surfactants, more particularly alkoxyated tallow amine surfactants, and possibly ammonium sulfate. The additives disclosed are said to enhance visibly the glyphosate activity. The formulations disclosed are said to show low toxicity characteristics against the organisms, partially due to lower content of surfactant.

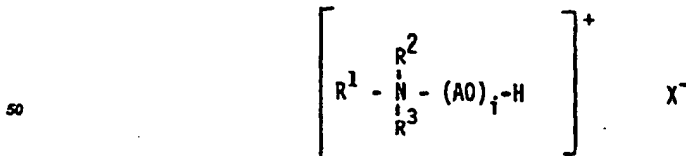
We have discovered that certain polyoxyalkylene quaternary ammonium compounds (disclosed hereinafter) are very effective in enhancing the herbicidal activity of glyphosate, and that improved glyphosate formulations containing such quaternary ammonium compounds are relatively non-toxic and non-irritant. We have also found that our new glyphosate formulations provide reduced foaming in comparison with known glyphosate formulations.

US-A-3 141 905, US-A-3 123 641 and US-A-3 123 640 disclose some particular polyoxyalkylated quaternary ammonium surfactants. The use of these types of surfactants in glyphosate compositions is however not disclosed nor suggested. Further, no toxicity or irritancy data in herbicide compositions are disclosed.

British patents No. 1 421 133, 1 462 043, 1 470 618, 1 450 531, 1 453 443, EP-A-0 066 946, WO-87/04595, GB-A-2 113 093, GB-A-2 059 773 and GB-A-2 047 098 disclose quaternary ammonium surfactants in pesticide formulations, but none of them discloses or suggests applicant's composition of glyphosate herbicide with a quaternary ammonium surfactant(s) disclosed herein.

European patent No. 0 206 537 discloses the use of Emcol-CC 57, a polypropoxyated quaternary ammonium surfactant, in solid phytoactive glyphosate compositions.

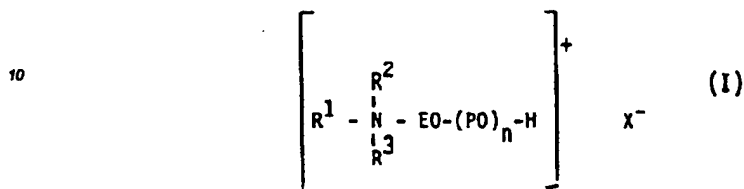
A composition of the invention comprises a glyphosate herbicide and a quaternary ammonium compound having the formula :



wherein A or each A represents an alkylene group having 2 or 3 carbon atoms, R<sup>1</sup> and R<sup>2</sup> are each independently an alkyl group having from 1 to 5 carbon atoms; R<sup>3</sup> is an alkyl group having from 1 to 5 carbon atoms or a group having the formula (AO)<sub>j</sub>-H; i (in a compound in which R<sup>3</sup> is an alkyl group) or i + j (in a compound

In which R<sup>3</sup> is a group having the formula (AO)<sub>r</sub>-H has a value of from 2 to 20 ; and X<sup>-</sup> is a suitable anion.

A preferred composition of the invention comprises a glyphosate herbicide and a quaternary ammonium compound the latter having a structure represented by the formula :



wherein -EO- is an ethylene oxide radical and -PO- is a propylene oxide radical, R<sup>1</sup> and R<sup>2</sup> are each independently an alkyl group having from 1 to 3 carbon atoms ; R<sup>3</sup> is an alkyl group having from 1 to 3 carbon atoms, a group having the formula (EO)<sub>m</sub>-H or a group having the formula EO-(PO)<sub>m</sub>-H ; n (in a compound in which R<sup>3</sup> is an alkyl group) or n + m (in a compound in which R<sup>3</sup> is a group having the formula EO-(PO)<sub>m</sub>-H), has a value of from 2 to 20 ; and X<sup>-</sup> is a suitable anion and n and m are each independently varying integers.

By a "suitable" anion is meant an anion such that applicant's composition is classified both as "non-irritant" when evaluated by a standard test procedure involving dermal and ocular tissue of the rabbit, and as "relatively non-toxic" to fish when evaluated by standard test procedures both hereinafter identified.

The compositions of this invention containing quaternary ammonium compounds as disclosed herein are non irritant and have relatively low toxicity. For example, they are less irritant and less toxic than compositions containing a glyphosate herbicide and a comparable amount of an ethoxylated fatty amine surfactant, one of the classes of surfactant(s) previously considered optimum for glyphosate enhancement.

Compared to alkyl polyglycoside surfactants known for their low eye irritancy characteristics in cosmetics for instance, and previously disclosed in liquid glyphosate compositions (see EP-A-0 220 902 and EP-A-0 364 202) the formulations according to our present invention provide comparatively much reduced foaming. Our invention reduces or eliminates the need for an antifoam ingredient such as a silicone antifoam agent. Without antifoam in the formulation, the need to shake the formulation of this invention before use is reduced or eliminated. This is of especial advantage when the formulation is to be sold in large containers.

Furthermore the compositions of our invention provide stable tank mixing with other pesticides and particularly herbicides. More especially the compositions according to the invention show good compatibility with triazines.

The number of propylene oxide units of the quaternary amine symbolized in Formula (I) is preferably in the range from 2 to about 20 as the advantages of this invention are more pronounced in that range.

Herein, the term "glyphosate herbicide" means N-phonomethylglycine (glyphosate) and any form or derivative of glyphosate which in aqueous solution provides glyphosate anions. Suitable cations may also be present.

Examples of such suitable cations are alkali metal cations, for instance sodium and potassium, and ammonium and substituted ammonium cations. The latter include cations derived from primary or secondary amines such as isopropylamine or dimethylamine, and from diamines such as ethylenediamine.

Especially preferred as a glyphosate herbicide are water soluble salts of glyphosate such as the isopropylamine salt of glyphosate and the trimethylsulfonium salt of glyphosate. US Patent 3,799,758 discloses salts of glyphosate useful herein. Other examples of agriculturally acceptable salts of glyphosate are aminoguanidine salts as disclosed in EP-A-0 088 180. Because glyphosate has more than one replaceable hydrogen atom, mono- and di- alkali metal salts are possible, as well as mixtures of such salts.

Especially preferred quaternary ammonium compounds for use in the present invention are those having a structure of Formula (I) wherein n has a value from 4 to 15 or n + m has a value from 3 to 14 and -PO- is isopropylene oxide.

quaternary ammonium compounds available in practice are not necessarily pure compounds in the sense of consisting of a single molecular species. In any particular instance, several different compounds where n or n and m vary over a narrow range will normally be present, so that the values of n and n + m mentioned above are understood as average values.

The anion symbolized as X<sup>-</sup> in Formula (I) symbolizing a quaternary ammonium compound used in a composition of the invention can be for example a halide ion, for instance chloride or bromide, phosphate, or methylsulphate, or ethylsulphate, or a a glyphosate ion. Other suitable anions include acetate, lactate, dimethyl

phosphate or polyalkoxylated phosphate and the like.

Particularly good results have been obtained with quaternary ammonium compounds having the above  
 5 general Formula (I) wherein  $R^1$  and  $R^2$  are each methyl,  $X^-$  is  $Cl^-$ , and where (i)  $R^3$  is  $EO-(PO)_m-H$  and  $n + m$  has an average value of about 6; (ii)  $R^3$  is methyl, and  $n$  has an average value of 6.3; or (iii)  $R^3$  is methyl and  $n$  has a value of about 8.

In the compositions of this invention, the weight ratio of glyphosate (expressed as glyphosate acid equivalent) to the quaternary ammonium compound can vary over a considerable range, for example from about  
 10 1:5 to about 10:1. The optimum ratio will vary according to the manner in which the herbicidal composition is applied, the weed species to be treated, and the particular quaternary ammonium compound selected, but is normally within the range from about 1:2 to about 4:1, for example about 1:1 or about 2:1.

A composition of the invention can be a liquid aqueous concentrate intended to be diluted with water to form a spray solution for the actual herbicidal application. A liquid concentrate will normally contain at least 50  
 15 grams glyphosate acid equivalent per litre, and preferably at least 100 g/l. Compositions of the invention may include a significant amount of an agriculturally-acceptable inorganic ammonium salt such as ammonium sulphate, in addition to the glyphosate and quaternary ammonium compound. Liquid concentrates without such an inorganic ammonium salt can contain up to 450 g/l or more, for example 300-450 g/l, glyphosate acid equivalent when the glyphosate is present as a salt having a high solubility, for example the isopropylamine salt. In  
 20 liquid concentrates containing an inorganic ammonium salt (for example ammonium sulphate in an amount of from 100 to 500 g/l), the maximum amount of glyphosate which can be accommodated is less, and may be, for example, about 150 g/l glyphosate acid equivalent.

In another form, a composition of the invention is a solid, for example a free-flowing particulate, granular solid or compressed into tablets or briquets of any desired size and shape. The term "solid" as employed herein  
 25 includes granular, particular, wettable powder, water soluble and water dispersible, mixtures thereof and the like. Typically such solids are dry. Such dry compositions will usually contain not more than 5% and preferably not more than 1% by weight of water.

In a solid composition, glyphosate is preferably present as the isopropylamine salt or an alkali metal salt such as a sodium or potassium salt, or as an ammonium salt. The surfactant used in the compositions of the  
 30 invention is particularly suitable for dry formulations.

Optionally solid compositions may be formulated to include a water-soluble inert carrier, and for this purpose ammonium sulphate is particularly suitable. The weight ratio of glyphosate (expressed as glyphosate acid equivalent) to quaternary ammonium compound in such compositions will be within the general range mentioned above. The amount of water-soluble inert carrier is not critical, and in the case of ammonium sulphate,  
 35 the amount may, for example, range from 20% to 80% of the total weight of the composition. Solid compositions can be made, for example by spray drying an aqueous solution of the components, by dry-blending the ingredients in conventional blending apparatus, or by extrusion blending whereby a granular product is obtained in an essentially single operation. In a preferred method, an alkali metal salt of glyphosate is prepared *in situ* by the method of European patent application 8790 1321.7. It has been found that by radial extrusion, a product  
 40 is obtained with better dissolution characteristics in water compared to a product with frontal extrusion.

Compositions of the invention also include solutions which may be applied by spraying for example. In these solutions, the concentration of glyphosate is selected according to the volume per unit area of spray solution to be used and the desired rate of application of glyphosate per unit area. For example, conventional spraying  
 45 is done at 100-600 litres of spray solution per hectare, and the rate of application of glyphosate is typically 0.125 to 1.5 kg of glyphosate acid equivalent per hectare. In controlled drop spraying, the rate of application of glyphosate per hectare will normally be in the same range, but the volume of spray solution per hectare will be considerably less, perhaps 15-50 litres per hectare. Spray solutions for controlled drop spraying are therefore more concentrated than those used in conventional spraying. In spray solutions containing inorganic ammonium salts in addition to the glyphosate and quaternary ammonium compound, the amount of inorganic ammonium salt  
 50 which can be included may be, for example, up to 10 times the weight of glyphosate acid equivalent.

Spray solution compositions can be prepared by diluting liquid concentrates or dissolving solid compositions as described above, or by tank mixing the separate components of the compositions.

Compositions of the invention can optionally contain other components, preferably those which do not have an adverse effect on the resulting composition as to irritancy and toxicity. These additional components may  
 55 include anti-freeze agents such as ethylene glycol, polyethylene glycols and glycerol. Other examples of additional components are dyes, thickening agents, anti-foam agents, for instance silicone-based anti-foam agents, agents suitable for pH adjustment to optimize herbicidal efficacy and stability of the composition, and certain surfactants, for instance non-ionic surfactants such as polyoxy-ethylene ethers or esters, and sugar ethers. Concentrates and solutions of the invention may also be mixed with one or more herbicides, themselves preferably having low or no irritancy and relatively low toxicity.

Some of the quaternary ammonium compounds shown in Table 1 following were used to prepare compositions in turn used in investigating their potentiating effect on the herbicidal action of glyphosate.

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TABLE 1

10	Quaternary Amine					Average
	No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	X <sup>-</sup>	n + m
	1	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	Cl <sup>-</sup>	8
	2	CH <sub>3</sub>	CH <sub>3</sub>	-EO-(PO) <sub>m</sub> -H	Cl <sup>-</sup>	6
15	3	CH <sub>3</sub>	CH <sub>3</sub>	-EO-(PO) <sub>m</sub> -H	Cl <sup>-</sup>	8
	4	CH <sub>3</sub>	CH <sub>3</sub>	-EO-(PO) <sub>m</sub> -H	Cl <sup>-</sup>	9.7
	5	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Cl <sup>-</sup>	6.3
20	6	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Cl <sup>-</sup>	8
	7	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub> SO <sub>4</sub> <sup>-</sup>	8.4
	8	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Cl <sup>-</sup>	3
	9	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Cl <sup>-</sup>	14.2
25	10	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	CH <sub>3</sub> SO <sub>4</sub> <sup>-</sup>	8
	11	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub> COO <sup>-</sup>	8
	12	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	PO <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	8
30	13	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Lactate	8
	14	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Cl <sup>-</sup>	20
	15	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Cl <sup>-</sup>	8
35	16	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	Cl <sup>-</sup>	7

Table 2 below shows the components and their concentrations in examples of prepared compositions of the invention which are liquid concentrates. The glyphosate is employed in the compositions as the isopropylamine salt of glyphosate, and the concentration of the isopropylamine salt glyphosate is expressed as glyphosate acid equivalent (a.e.).

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TABLE 2

COMPOSITION No.	QUATERNARY AMINE		GLYPHOSATE A.E.
	No.	Conc. (g/l)	Conc. (g/l)
1	2	180	360
2	2	200	400
3	2	225	450
4	5	180	360
5	5	200	400
6	5	225	450
7	6	180	360
8	6	200	400
9	6	225	450

g/l = grams per litre.

Examples of two solid compositions of this invention are shown in Table 3 below.

TABLE 3

Components	Composition No.	
	10	11
( % by weight )		
Glyphosate sodium salt	24.03	39.48
Quaternary amine No. 6 (TABLE I)	10.63	17.50
Ammonium sulphate	63.79	40.80
Silicone defoamer	0.08	0.12
Water	0.50	0.50
Inert(s)	0.97	1.60

The herbicidal effectiveness of spray solutions prepared by the dilution of some of the liquid concentrates exemplified above was evaluated as follows :

For greenhouse tests, plants were grown from seed in 13 cm pots containing a natural sandy loam soil enriched with a mixture of fertilizer. All irrigation was supplied automatically from below. The environment was controlled at a temperature regime of 18°C (day), 12°C (night), a relative humidity of 65% day and 75% night, and an illuminance of 1500 microeinsteins m<sup>-2</sup>s<sup>-1</sup> (with an artificial shading if natural light gave more, and an artificial supply if the natural light was less than 1300 microeinstein m<sup>-2</sup>s<sup>-1</sup>).

Before spraying, pots were selected for uniformity as far as possible, and atypical examples were discarded. Spray solutions were applied with a Mardrive precision laboratory sprayer, calibrated to deliver spray solution in one pass at a rate equivalent to 200 l/ha. All replicate pots (3-5 replicates per species, per treatment) were sprayed with one pass of the sprayer.

After treatment, control pots were placed at random among treated pots. Assessments of "% phytotoxicity" were made by comparison with untreated controls and with Controls\* sprayed with a glyphosate solution containing an ethoxylated tallow amine surfactant in a weight ratio of 2 : 1 glyphosate a.e. : surfactant, on an arbitrary scale from 0 to 100%, where 0 means no visible effect and 100% means death of all plants. For any one assessment, all pots were rated by the same individual, assessments being performed "blind", without knowledge of the treatment.

Results were as follows. The results in Table 4 for % phytotoxicity represent the average of 3 rates (200,

400 and 600 g glyphosate a.e./ha) x 3 replicates, 34 days after treatment for each quaternary amine (designation from Table 1).

TABLE 4

Quaternary No.	<u>Lolium multiflorum</u>	<u>Geranium molle</u>
1	32	36
2	45	47
3	29	35
4	32	36
5	46	51
6	44	45
Control*	34	41

The results in Table 5 for the % phytotoxicity are the average of 3 rates (200, 400 and 600 g glyphosate a.e./ha) x 3 replicates, 30 days after treatment.

TABLE 5

<u>Quaternary No.</u>	<u>Elymus repens</u>
2	43
3	39
4	52
6	55
Control *	46

A field test was carried out in a sown 90 m<sup>2</sup> pasture containing a mixture of perennial ryegrass and black-grass for the narrow leaved species (grasses) and a mixture of *Sinapis arvensis* *Matricaria* sp. and *Trifolium repens* broadleaves. This was sprayed at a spray volume application rate equivalent to about 400 l/ha, and at an air temperature of about 18°C. No rain was noted for 5 days after spraying. The test design was a complete randomized block design with 3 replicates of each treatment and one untreated plot per 4 treated plots. The results in Table 6 below for the % phytotoxicity are the average of 3 rates (800, 1200 and 1600 g glyphosate a.e./ha) x 3 replicates, 30 days after treatment.

TABLE 6

Quaternary No.	Grasses	Broadleaves
2	45	49
6	40	45
Control*	42	47

Compositions containing the quaternary Nos. 2, 5 and 6 of this invention in these tests (Table 4, 5 and 5)

show comparable efficacy to the Control" composition therein. Thus in considering these data, these phytotoxicity tests show that Quaternaries Nos. 2, 5 and 6 enhanced the performance of glyphosate to a similar degree as did the ethoxylated fatty amine surfactant of the Control.

Standard skin and eye irritancy tests were carried out using compositions Nos. 2, 5 and 8 on New Zealand white rabbits by the procedures of OECD Guidelines for Testing of Chemicals, Tests No. 404 "Acute Dermal Irritancy/Corrosion", 12 May 1981, and 405 "Acute Eye Irritancy/Corrosion" 24 February 1987, respectively. When the results were assessed according to the criteria of European Commission Directive 83/467/EEC, all the compositions were classified as non-irritant to both dermal and ocular tissue.

The same compositions were examined for toxicity to fish by the procedure of OECD Guidelines for Testing of Chemicals, Test No. 203, 4 April 1984, "Fish Acute Toxicity Test". When the results were assessed on the Proposed Toxicity Rating Scale for Use at CNFRL (Columbia National Fisheries Research Laboratory, U.S.A.) the compositions were classified as "relatively non-toxic".

Quaternary amines designated in Table 1 as numbers 6-10 were tested in another field test in Summer. The rates of glyphosate (as glyphosate isopropylamine salt) application were equivalent to about 300, 600 and 900g a.a./ha. The application was made at about 250 l/ha using standard field spraying equipment. The ratio of glyphosate acid equivalent surfactant was about 2/1. The weed assessed is Trifolium repens (TRFRE).

The weather at the spraying was clear and hot, no wind. Temperature was around 30°C and no rain was recorded in six hours following spraying.

Assessment of per cent phytotoxicity was made by comparison with untreated control plots on an arbitrary scale from 0 to 100%, where 0 means no visible effect and 100 means death of all plants.

Randomised block design with 3 replicates was used (1 check per 5-6 treatment plots). Unit plot size = 1.5m x 3.5m.



TABLE 7

Quaternary Amine No	Glyphosate g. a.e./ha	TRFRE 32 DAT <sup>XXX</sup>
Control*	300	35
	600	47
	900	53
6	300	25
	600	38
	900	55
7	300	27
	600	38
	900	50
10	300	23
	600	35
	900	47
9	300	25
	600	48
	900	50
8	300	18
	600	33
	900	45

DAT<sup>XXX</sup> = days after treatment.

The quaternary amines numbered 6-10 in TABLE 2 in a series of 2/1 glyphosate acid equivalent/surfactant compositions were also tested in a further greenhouse test. The conditions were the same as previously. The rates of application were 360, 540 and 1080 g a.e./ha (glyphosate in the form of the isopropylamine salt).

Results are shown in table 8.

TABLE 8

Quater- nary No.	Rate g a.e. /ha	BRSNW (DAT)			GERMO (DAT)			LOLRI (DAT)		AGGRE (DAT)	
		14	20	36	14	20	36	20	36	20	36
7	360	17	27	39	15	60	85	47	77	70	90
	540	23	38	58	35	70	93	92	100	75	82
	1080	47	63	78	40	75	98	83	100	77	100
10	360	30	42	42	27	65	80	55	85	60	82
	540	47	55	65	43	73	88	67	92	75	87
	1080	45	62	75	55	78	95	99	100	78	100
9	360	30	23	35	15	33	60	58	82	63	75
	540	37	55	58	50	60	75	60	93	73	93
	1080	53	78	95	53	65	78	88	100	83	100
8	360	10	20	8	10	35	75	50	85	47	73
	540	25	20	12	33	63	95	63	97	70	87
	1080	28	45	60	48	73	100	80	98	82	97
6	360	12	20	33	15	70	80	52	87	77	93
	540	30	40	52	40	65	85	83	95	85	100
	1080	37	68	83	50	70	90	83	98	82	98
Control*											
	360	17	20	37	8	35	65	62	92	65	80
	540	42	57	65	40	68	100	87	100	85	100
	1080	50	67	75	58	80	100	93	100	73	100
The assessed weeds are:											
	BRSNW	Brassica (oil seed rape)									
	GERMO	Geranium molle									
	LOLRI	Lolium rigidum									
	AGGRE	Agropyron repens (couch)									

The results are shown in the previous Tables 7 and 8 indicate that the glyphosate phytotoxicity of compositions of the invention employed herein is enhanced to a level comparable to that of the Control\* composition. Compositions of the invention are particularly compatible with other herbicides and show good stability charac-

teristics when mixed with one or more other herbicides. Also tank mix properties appeared very good. In a compatibility test, the following formulations were used :

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10	Composition	Ingredient	Amount of Composition Employed with Ingredient
	(1)	Glyphosate + Quaternary amine (2)	6L <sup>XX</sup> in 400L
15	(7)	Glyphosate + Quaternary amine (6)	6L in 400L
	GESATOPE	Simazine	6L in 400L
	CENT - 7	Isoxaben	8L in 400L
20	SEXTAN	Isoxaben/Simazine	7.5L in 400L
	VITIDOR	Oryzalin/Simazine	12L in 400L
	FENICAN	Diuron/Terbuthylazine	6L in 400L
	ZORIAL	Norflurazon	2.5kg in 400L
25	GOLTIX	70% Metamitron	5kg in 400L
	PYRAMIN	65% Chloridazon	5kg <sup>XXX</sup> in 400L

30 The coherbicide was mixed with water and then composition (1) or  
(7) was added and the mixture thoroughly mixed. Observations were  
made at 1, 5, 10, 30 and 60 minutes after mixing. Final  
35 evaluation was done after two hours. No compatibility agent was  
added.

40 L<sup>XX</sup> = liter  
kg<sup>XXX</sup> = Kilogram

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## COMPATIBILITY TEST

MIXTURE No.	after 1 min.	after 5 min.	after 10 min.	after 30 min.	after 60 min.	after 2 hours
(1) + Gesatope	OK	OK	OK	sed/red	Sed/red	Sed/red
(1) + Cent - 7	OK	OK	OK	OK	Sed/red	Sed/red
(1) + Sextan	OK	OK	OK	OK	Sed/red	Sed/red
(1) + Vitidor	OK	OK	OK	OK	Sed/red	Sed/red
(1) + Fenican	OK	OK	OK	OK	Sed/red	Sed/red
(1) + Zorial	OK	OK	OK	OK	Sed/red	Sed/red
(1) + Goltix	OK	OK	OK	OK	Sed/red	Sed/red
(1) + Pyramin	OK	OK	OK	OK	Sed/red	Sed/red
(7) + Gesatope	OK	OK	OK	Sed/red	Sed/red	Sed/red
(7) + Cent-7	OK	OK	OK	OK	Sed/red	Sed/red
(7) + Sextan	OK	OK	OK	OK	Sed/red	Sed/red
(7) + Vitidor	OK	OK	OK	OK	Sed/red	Sed/red
(7) + Fenican	OK	OK	OK	OK	Sed/red	Sed/red
(7) + Zorial	OK			Tr.sed	Sed/red	Sed/red
(7) + Goltix	OK	OK	OK	Sed/red	Sed/red	Sed/red
(7) + Pyramin	OK	OK	OK	OK	Sed/red	Sed/red

OK = No Compatibility Problems

Tr.sed = Trace of Sedimentation

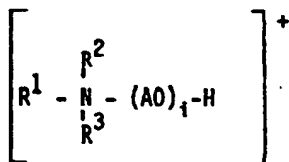
Sed/red = Sedimentation but Easily Re-dispersible

min. = Minutes

As an advantage, compositions of this invention may contain suitable coherbicides including sulfonyl ureas depending on the intended use of the composition containing the coherbicide(s).

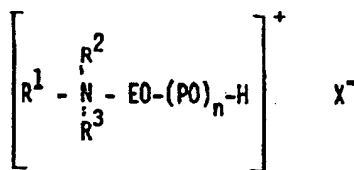
## Claims

1. A composition of the invention comprises a glyphosate herbicide and a quaternary ammonium compound having the formula :



wherein A or each A represents an alkylene group having 2 or 3 carbon atoms, R<sup>1</sup> and R<sup>2</sup> are each independently an alkyl group having from 1 to 5 carbon atoms ; R<sup>3</sup> is an alkyl group having from 1 to 5 carbon atoms or a group having the formula (AO)<sub>j</sub>-H ; i (in a compound in which R<sup>3</sup> is an alkyl group) or i + j (in a compound in which R<sup>3</sup> is a group having the formula (AO)<sub>j</sub>-H) has a value of from 2 to 20 ; and X<sup>-</sup> is a suitable anion.

2. A composition comprising a glyphosate herbicide and a quaternary ammonium compound the latter having the formula



wherein -EO- means an ethylene oxide radical and -PO- means a propylene oxide radical, R<sup>1</sup> and R<sup>2</sup> are each independently an alkyl group having from 1 to 3 carbon atoms ; R<sup>3</sup> is an alkyl group having from 1 to 3 carbon atoms, a group having the formula (EO)<sub>m</sub>-H or a group having the formula EO-(PO)<sub>m</sub>-H ; n (in a compound in which R<sup>3</sup> is an alkyl group) or n + m (in a compound in which R<sup>3</sup> is a group having the formula EO-(PO)<sub>m</sub>-H), has a value of from about 2 to about 20 ; and X<sup>-</sup> is a suitable anion.

3. A composition according to Claim 2 wherein, in the formula of the quaternary ammonium compound, -PO- means isopropylene oxide and n (in a compound in which R<sup>3</sup> is a methyl or ethyl group) has a value of from 4 to 15, and n + m (in a compound in which R<sup>3</sup> is a group having the formula EO-(PO)<sub>m</sub>) has a value of from 3 to 14 and X<sup>-</sup> is halide, ethylsulfate, methylsulfate, dimethylphosphate, polyalkoxyphosphate, lactate or acetate.
4. A composition according to Claim 3 wherein R<sup>1</sup> and R<sup>2</sup> are each methyl, X<sup>-</sup> is Cl<sup>-</sup>, and where (i) R<sup>3</sup> is EO-(PO)<sub>m</sub>-H and n + m has a value of about 6 ; or (ii) R<sup>3</sup> is methyl, and n has an average value of 6.3 ; or (iii) R<sup>3</sup> is methyl and n has a value of about 8.
5. A composition according to any of Claims 1 to 4 in which the weight ratio of glyphosate (expressed as glyphosate acid equivalent) to the quaternary ammonium compound is in the range from about 1 :2 to about 4 :1.
6. A composition according to any of Claims 1 to 5 in which the glyphosate is present as the isopropylamine salt or the trimethylsulfonium salt of glyphosate.
7. A composition according to any of Claims 1 to 6 which is a liquid concentrate containing at least 100 g/l of glyphosate expressed as glyphosate acid equivalent.
8. A composition according to any of Claims 1 to 5 in which the glyphosate is present as an alkali metal or ammonium salt.
9. A composition according to Claim 8 in which the glyphosate is present as a sodium salt.
10. A composition according to either of Claims 8 and 9 which is a solid composition.
11. A composition according to Claim 10 which includes a water-soluble inert support.
12. A composition according to Claim 11 in which the water-soluble inert support is ammonium sulphate in an amount of from 20% to 80% of the total weight of the composition.
13. A composition according to any of Claims 1-12 which further contains anti-freeze agents and/or dyes and/or thickening agents and/or anti-foam agents and/or co-surfactants.

- 5 14. A composition according to any of Claims 1-12 which further contains a co-herbicide selected from Simazine, Isoxaben, Oryzalin, Diuron, Terbutylazine, Norflurazon, Metamitron, Chloridazon or sulfonyl urea in an agriculturally effective amount.
- 15 15. A composition according to any of Claims 1-13 where an agriculturally effective amount of glyphosate is present along with an effective amount of said quaternary amine composed of said formula.
- 10 16. A composition according to any of Claims 1 to 6 and 12, 13 which is a spray solution having a concentration such that when sprayed at 100 - 600 litres per hectare, 0.125 to 1.5 kg of glyphosate (expressed as glyphosate acid equivalent) per hectare is applied.
- 15 17. Use of a composition according to any of Claims 1-15 as a growth regulating agent or herbicide for killing narrow leaved and/or broadleaved unwanted vegetation in a rate of 0.125 and 1.5 kg glyphosate acid equivalent per hectare.
- 20 18. A process for the preparation of a dry solid composition of Claim 1 by spray drying an aqueous solution of the components, by dry-blending the ingredients or by extruding the ingredients of the compositions.
- 25 19. Use of a quaternary ammonium compound as shown in Claims 1-16 as a tank mix adjuvant to form a herbicidal composition containing glyphosate.
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EP 0 441 764 A1



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 91 87 0016

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 357 553 (CIBA-GEIGY) * Page 5, lines 10-25; claims *	1	A 01 N 57/20 A 01 N 25/30 //
A	EP-A-0 274 369 (MONSANTO CO.)		(A 01 N 57/20 A 01 N 25:30 )
D,A	US-A-3 141 905 (K. LONGLEY)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A 01 N
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15-05-1991	Examiner DONOVAN T.M.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : oral-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>A : number of the same patent family, corresponding document</p>			

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